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(54) PHOTOCATALYTIC COATING MATERIAL COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a coating material containing photocatalytic particles, a binder and a solvent, and capable of simply and easily forming photocatalytic membrane having excellent photocatalytic function on the surface of an article, and further to provide an article on which photocatalytic membrane having excellent photocatalytic function is formed.

SOLUTION: This photocatalytic coating material composition is prepared by including (A) at least one kind of compounds selected from the group consisting a dicarboxylic acid and its derivative, (B) photocatalytic particles, (C) a binder and (D) a solvent. This article on which photocatalytic membrane having excellent photocatalytic function is formed is produced by applying or straying the photocatalytic material composition to the surface of an article and then drying it.

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CLAIMS

[Claim(s)]

[Claim 1] The light catalytic coating constituent characterized by coming at least to contain a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative, a photocatalyst particle, a binder, and a solvent.

[Claim 2] The light catalytic coating constituent according to claim 1 with which the content of at least a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative is characterized by being 0.5 - 500 % of the weight to a photocatalyst particle.

[Claim 3] The light catalytic coating constituent according to claim 1 characterized by the content of a photocatalyst particle being 0.01 - 10 % of the weight.

[Claim 4] The light catalytic coating constituent according to claim 1 characterized by a photocatalyst particle being titanium oxide which has the mean particle diameter of the range of 1-500nm.

[Claim 5] The light catalytic coating constituent according to claim 1 with which a binder is characterized by being the hydrolysis product of a hydrolysis nature silicon compound.

[Claim 6] A hydrolysis nature silicon compound is $\text{Si}_n\text{O}_{n-1}$. Light catalytic coating constituent according to claim 5 characterized by being alkyl silicate expressed with $(\text{OR})_{2n+2}$ (a carbon number 1-6R, as for however, n alkyl group of 1-4).

[Claim 7] The light catalytic coating constituent according to claim 1 characterized by a solvent being the thing which comes to contain alcohol.

[Claim 8] Goods characterized by coming to form the photocatalyst film on the front face of goods using a light catalytic coating constituent according to claim 1.

[Claim 9] The manufacture approach of the goods which come to form the photocatalyst film which applies a light catalytic coating constituent according to claim 1 on the surface of goods, or sprays, carries out, and is subsequently characterized by drying.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the goods in which the light catalytic coating constituent for using for formation of the photocatalyst film and the photocatalyst film were formed, and its manufacture approach.

[0002]

[Description of the Prior Art] If the light which has the energy more than the band gap in titanium oxide is irradiated, optical pumping will be carried out and an electron hole and an electron will be generated on a titanium oxide particle front face. Since the electron hole produced especially on the titanium oxide particle front face has very powerful oxidizing power, it can remove deleterious material, such as harmful matter, a malodorous substance, stimulative matter, an environmental pollutant, mold, algae, and bacteria. Thus, if light is irradiated, generally a photocatalyst function, a call, and recent-years research are briskly done in the aforementioned deleterious material removal function which discovers the matter which the electron of a valence band excites by the photocatalyst, the call, and optical pumping. Furthermore, using this photocatalyst function, the front face of goods is made into a hydrophilic property, that it is hard to adhere dirt, it can carry out, or cloudiness can also be prevented, and the application scene of a photocatalyst is spreading.

[0003] Although a photocatalyst is used according to each application in the condition of fine particles, the condition of a Plastic solid, the condition of the sol which distributed the photocatalyst, and the condition of having fixed to the front face of goods, it is used in many cases in the condition of having fixed to the front face of goods from the merit of handling, like scattering and the outflow from the system of reaction being prevented. Furthermore, to use the aforementioned hydrophilization function, it is necessary to form and fix the photocatalyst film in homogeneity on the surface of goods. In order to fix a photocatalyst, since the light catalytic coating constituent which made the binder and the solvent distribute a photocatalyst particle can be applied on the surface of goods or the approach which has sprayed enough and is carried out can form the photocatalyst film in homogeneity, it is a desirable approach.

[0004]

[Problem(s) to be Solved by the Invention] If the photocatalyst film is formed using the aforementioned light catalytic coating constituent which comes to contain a photocatalyst particle, a binder, and a solvent, a photocatalyst particle is easy to be covered with a binder, and may be unable to discover an original photocatalyst function easily, and the further improvement is called for.

[0005]

[Means for Solving the Problem] When this invention persons made a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative as a result of examining many things, in order to create the photocatalyst film which can discover the further excellent photocatalyst function, the photocatalyst particle, the binder, and the solvent contain at least and considered as the light catalytic coating constituent, they completed a header and this invention for the desired photocatalyst film being obtained. That is, this invention is to offer the light catalytic coating constituent which forms the photocatalyst film which has the outstanding photocatalyst function. Furthermore, it is in offering the goods which come to form the photocatalyst film using the light catalytic coating constituent, and its manufacture approach.

[0006]

[Embodiment of the Invention] This invention is a light catalytic coating constituent characterized by making it come at least to contain a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative, a photocatalyst particle, a binder, and a solvent. The light catalytic coating constituent of this invention can mix at least a kind of compound and photocatalyst particle which are chosen from the group which consists of dicarboxylic acid and its derivative, a binder, and a solvent with a conventional method, respectively, and can be manufactured.

[0007] A photocatalyst particle is a particle which will discover a photocatalyst function if the light of wavelength with the energy more than the band gap is irradiated, and well-known metallic-compounds semi-conductors, such as titanium oxide, a zinc oxide, tungstic oxide, ferrous oxide, and strontium titanate, can be used combining a single or two sorts or more. It has an especially high photocatalyst function and stable and harmless titanium oxide is chemically desirable. The range of 1-500nm is desirable, and the range which is 1-100nm is more desirable, and since the mean particle diameter of this titanium oxide has the photocatalyst function excellent in the range of 1-10nm, it is [its range which is 1-50nm is still more desirable, and] the most desirable. Furthermore, when at least a kind of metal chosen from the group which consists of V, Fe, Co, nickel, Cu, Zn, Ru, Rh, Pd, Ag, Pt, and Au as the second component on the interior of a photocatalyst particle and/or its front face, and/or metallic compounds are made to contain, since it has a still higher photocatalyst function, it is desirable. As the aforementioned metallic compounds, a metal ion etc. is included in a metal oxide, a hydroxide, an oxy-hydroxide, a sulfate, a halogenide, a nitrate, and a pan, for example. The content of the second component can be suitably set up with the matter. As a photocatalyst particle which makes an aforementioned metal and/or metallic compounds contain, titanium oxide is desirable. They are about 0.01 - 10 % of the weight, the loadings of a photocatalyst particle have 0.05 - 5 desirable % of the weight in a light catalytic coating constituent, its 0.1 - 5 % of the weight is more desirable to it, and its 0.1 - 1 % of the weight is still more desirable to it. Since it will be hard coming to form the photocatalyst film if [than the above-mentioned range] more [a photocatalyst function will tend to fall if there are few loadings of a photocatalyst particle than the above-mentioned range and], it is not desirable.

[0008] The photocatalyst particle used in this invention is obtained by the well-known approach. As an approach of obtaining titanium oxide, for example, ** sulfuric-acid titanium, sulfuric-acid titanyl. The need is accepted in titanium compounds, such as a

titanium chloride and a titanium alkoxide. Under existence of the seed for nucleation The approach and ** need which carry out heating hydrolysis are accepted. Under existence of the seed for nucleation Sulfuric-acid titanium, Alkali is added to titanium compounds, such as sulfuric-acid titanyl, a titanium chloride, and a titanium alkoxide. There is the approach of calcinating or hydrothermal processing the titanium oxide obtained by the approach of the approach of carrying out vapor phase oxidation of the approach and ** titanium chloride to neutralize, the titanium alkoxide, etc., the ** aforementioned **, and ** etc., and since especially the titanium oxide obtained by the approach of the aforementioned ** has the high photocatalyst function, it is desirable. In this invention, it is not asked that the crystal mold is titanium oxide including what is generally called water titanium oxide besides titanium oxide, hydration titanium oxide, metatitanic acid, an alt.titanic acid, hydroxylation titanium, etc. On the interior of a photocatalyst particle, and/or its front face, as the second component, V, In order to make at least a kind of metal chosen from the group which consists of Fe, Co, nickel, Cu, Zn, Ru, Rh, Pd, Ag, Pt, and Au, and/or metallic compounds contain In case a photocatalyst particle is manufactured, this metal and/or these metallic compounds are added. After manufacturing the approach and photocatalyst particle which are made to adsorb, add and this metal and/or these metallic compounds are made to adsorb, it can heat if needed or the approach which has returned enough and is carried out if needed can be used.

[0009] If the thing of the condition of a sol is used, since the smooth photocatalyst film and the photocatalyst film with high transparency will be easy to be obtained, a photocatalyst particle is desirable. For example, in order to obtain a titanium oxide sol, amalgam-decomposition processing of the titanium oxide, such as (1) water titanium oxide, can be carried out with a monobasic acid and its salt, or after adding (2) titanium tetrachlorides in low-temperature water, it can dialyze, or a titanium alkoxide can be added in (3) hydrochloric-acid water solutions, and it can obtain. In the approach of the above (1), water titanium oxide can carry out heating hydrolysis of the titanium compounds, such as water-soluble inorganic titanium compounds, such as for example, sulfuric-acid titanium, sulfuric-acid titanyl, and a titanium tetrachloride, or adds alkali, such as a sodium hydroxide, a potassium hydroxide, and aqueous ammonia, in a titanium compound water solution, neutralizes, and can be obtained. The water titanium oxide obtained by hydrolyzing usually neutralizes this thing with alkali, after it removes solid liquid separation and the sulfuric-acid root which washes, dehydrates and remains inside as much as possible, adds monobasic acids, such as a hydrochloric acid, a nitric acid, an acetic acid, a chloric acid, and the Krol acid, or the salt of those to this dehydrate, and carries out amalgam-decomposition processing. The titanium oxide sol generated by amalgam-decomposition processing contains a monobasic acid or its salt as a distributed stabilizing agent, and usually shows with a pH of three or less acidity. The particle diameter of a titanium oxide particle can be made more detailed by performing heating hydrolysis, lowering neutralization temperature, or making neutralization late. Thus, if alkali is gradually added to a stable titanium oxide sol by pH of the obtained acid range and pH is raised, a stable titanium oxide sol will be obtained by pH of a neutral region and an alkaline region. An impurity is also removable from the titanium oxide sol of the obtained neutral region and an alkaline region if needed.

[0010] The product obtained as a binder by, for example, hydrolyzing hydrolysis nature silicon compounds, such as alkyl silicate, halogenation silicon, and these partial hydrolysates, Silicon compounds, such as a silica, colloidal silica, water glass, and organopolysiloxane, Phosphate, such as phosphoric-acid zinc and aluminium phosphate, heavy phosphate, cement, A kind of binders, such as organic system binders, such as inorganic system binders, such as lime, gypsum, a frit for enamels, glaze for glass lining, and plaster, a fluorine system polymer, and a silicone system polymer, or two sorts or more may be blended. A binder needs to choose the class of binder suitably according to a use scene, and extent and application of a photocatalyst function, in order to deteriorate by the photocatalyst function of a photocatalyst or to decompose. Since the rate of degradation by the photocatalyst function which a photocatalyst particle has, and decomposition is very slow as a binder, the hydrolysis product of hydrolysis nature silicon compounds, such as alkyl silicate, a silicone system polymer, and a fluorine system polymer are desirable. Alkyl silicate is $\text{Si}(\text{OR})_n$ as a general formula. The compound expressed with $(\text{OR})_{2n+2}$ (however, in Si silicon and O show oxygen and R shows an alkyl group.) is said, n is 1-6 and that [R's] whose carbon number is the alkyl group of 1-4 is more desirable at a point with many rates of silicon. They are converted into solid content and are about 10 - 2000 % of the weight to a photocatalyst particle, the loadings of a binder have 25 - 1000 desirable % of the weight, its 25 - 500 % of the weight is more desirable, and its 25 - 250 % of the weight is still more desirable. Since it will become easy for a photocatalyst function to fall if [than the above-mentioned range] more [when there were few loadings of a binder than the above-mentioned range and it considers as the photocatalyst film / a photocatalyst tends to **** and], it is not desirable.

[0011] As a solvent, an inorganic solvent or organic solvents, and those mixture can be used. As an inorganic solvent, water is desirable. As an organic solvent, alcohols, such as a methanol, ethanol, 2-propanol, and ethylene glycol, and ketones can be used. The thing which comes to contain alcohol from the point of handling nature and coating nature is desirable. The loadings of a solvent can be suitably set up according to workability.

[0012] The light catalytic coating constituent of this invention is made to contain at least a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative. Dicarboxylic acid is an organic compound which has two carboxyl group $\text{COOH}(\text{s})$ in intramolecular, for example, aromatic series dicarboxylic acid, such as aliphatic series partial saturation dicarboxylic acid, such as aliphatic series saturation dicarboxylic acid, such as oxalic acid, a malonic acid, a succinic acid, a glutaric acid, an adipic acid, a pimelic acid, a suberic acid, an azelaic acid, and a sebacic acid, a maleic acid, and a fumaric acid, a phthalic acid, isophthalic acid, and a terephthalic acid, etc. can be used. A dicarboxylic acid derivative is a compound which dicarboxylic acid, such as the esterification object of the aforementioned dicarboxylic acid, a salt of dicarboxylic acid, a dicarboxylic acid anhydride, dicarboxylic acid azide, a dicarboxylic acid amide, and dicarboxylic acid imide, has the change on the structure of an element, and is made into it, for example, dicarboxylic acid methyl, dicarboxylic acid ethyl, dicarboxylic acid propyl, dicarboxylic acid butyl, dicarboxylic acid sodium, dicarboxylic acid ammonium, etc. can be used. Moreover, trade name Rowdy ASORUBU (made in RO - NU PURAN Japan) which blended the goods containing dicarboxylic acid or its derivative, for example, three sorts of dicarboxylic acid ester, may be used. It is about 0.5 - 500 % of the weight to the photocatalyst particle in a light catalytic coating constituent, the content of dicarboxylic acid and its derivative has 5 - 500 desirable % of the weight, its 10 - 500 % of the weight is more desirable, and its 25 - 250 % of the weight is still more desirable. Since the remarkable effectiveness beyond it is hard to accept even if it will be hard to discover the addition effectiveness and will make [more] it than the above-mentioned range, if there are few contents of dicarboxylic acid and its derivative than the above-mentioned range, it is not desirable. In addition, it is guessed that the mechanism of action by containing dicarboxylic acid or its derivative can improve a photocatalyst function, especially a hydrophilization function when it is thought that there is an operation which makes the vapor rate of a solvent slow or promotes the cure rate of a binder as an acid catalyst although it is not yet clear and the photocatalyst film created using the light catalytic coating constituent containing dicarboxylic acid or its derivative becomes porosity. In addition, the light catalytic coating constituent of this invention may be made to contain various additives, such as a dispersant, a surfactant, a curing agent, and a

cross linking agent, in addition to at least a kind of compound and photocatalyst particle which are chosen from the group which consists of dicarboxylic acid and its derivative, a binder, and a solvent.

[0013] Next, they are the goods characterized by this invention coming to form the photocatalyst film on the front face of goods using the aforementioned light catalytic coating constituent. As goods, the goods of the metal quality of the materials, such as alloys, such as metals, such as goods of the organic quality of the materials, such as goods of quality of non-equipments, such as ceramics and glass, plastics, rubber, a tree, and paper, and aluminum, and a rope, can be used. It is not restricted to especially the magnitude or the form of goods. The thickness of the photocatalyst film formed on goods can be suitably set up according to an application, for example, can be made into the thickness which is about 0.01-100 micrometers. In order to form the photocatalyst film on goods using the light catalytic coating constituent of this invention It can carry out by applying or spraying a light catalytic coating constituent on goods. Specifically For example, the sinking-in method, a DIP coating method, a spinner coating method, A blade coating method, a roller coating method, a wire bar coating method, It can apply by the usual approaches, such as the reverse-roll-coating method, brush painting, and the sponge applying method, or can spray by the usual approaches, such as a spray coating method. Thus, after applying or spraying, it dries or calcinates and a solvent is removed. As for the temperature of desiccation or baking, it is desirable to carry out at temperature lower than 700 degrees C, and it is more desirable to carry out at the temperature which is room temperature -500 degree C. In this case, since it will become easy for a photocatalyst function to fall if higher than 700 degrees C, it is not desirable. It may decompose or the compound which is chosen from the group which consists of dicarboxylic acid and its derivative in the case of desiccation and baking and which a kind contained at least may evaporate. Furthermore, in order to solidify the used binder if needed, approaches, such as UV irradiation, may be used. In addition, before applying a light catalytic coating constituent to goods or spraying and making it them, by considering organic system binders and the aforementioned inorganic system binders, such as the aforementioned organic system binder, acrylic resin, an epoxy resin, polyester resin, melamine resin, urethane resin, and alkyd resin, as a primer or paint, it may apply to goods beforehand, or you may spray and carry out if needed.

[0014] The goods in which the photocatalyst film of this invention was formed are useful as a photocatalyst. Deleterious material, such as the toxic material which exists in the surroundings of it by making the light of wavelength with the energy more than the band gap of a photocatalyst irradiate, a malodorous substance, the stimulative matter, an environmental pollutant, a bacillus, mold, algae, and bacteria, is removable, and also the front face of goods is made into a hydrophilic property, dirt can be prevented or cloudiness can be prevented. The light containing ultraviolet rays etc. is mentioned as a light to irradiate, for example, light, such as sunlight, a fluorescent lamp, the black light, a halogen lamp, a xenon flash tube, and a mercury-vapor lamp, can be used. When using titanium oxide as a photocatalyst especially, the light containing a 300-400nm near ultraviolet ray is desirable. An exposure, irradiation time, etc. of light can be suitably set up with the class and amount of the matter to process.

[0015]

[Example] Although the example of this invention is shown below, this invention is not limited to these examples.

[0016] Succinic-acid dimethyl and isopropanol were added in the example 1 light catalytic coatings (ST-K03, Ishihara Sangyo [Kaisha, Ltd.] make: what blended the hydrolysis product of a hydrolysis nature silicon compound as a binder, and blended water and alcohol for the sol which contains titanium oxide with a mean particle diameter of 30nm as a photocatalyst as a solvent), and the light catalytic coating constituent (sample A) of this invention was obtained. Titanium oxide concentration is 2 % of the weight, and this sample A is the silicon in a silicon compound SiO₂ The converted amount (solid content) contained succinic-acid dimethyl 245% of the weight to titanium oxide 100% of the weight to titanium oxide.

[0017] In example 2 example 1, except having replaced with succinic-acid dimethyl and having used adipic-acid dimethyl, it processed like the example 1 and the light catalytic coating constituent (sample B) of this invention was obtained. Titanium oxide concentration is 2 % of the weight, and this sample B is the silicon in a silicon compound SiO₂ Adipic-acid dimethyl contained the converted amount (solid content) 245% of the weight to titanium oxide 100% of the weight to titanium oxide.

[0018] In example 3 example 1, except having replaced with succinic-acid dimethyl and having used glutaric-acid dimethyl, it processed like the example 1 and the light catalytic coating constituent (sample C) of this invention was obtained. Titanium oxide concentration is 2 % of the weight, and this sample C is the silicon in a silicon compound SiO₂ The converted amount (solid content) contained glutaric-acid dimethyl 245% of the weight to titanium oxide 100% of the weight to titanium oxide.

[0019] In example of comparison 1 example 1, except not using succinic-acid dimethyl, it processed like the example 1 and the light catalytic coating constituent (sample D) was obtained. Titanium oxide concentration is 2 % of the weight, and this sample D is the silicon in a silicon compound SiO₂ The converted amount (solid content) was contained 100% of the weight to titanium oxide.

[0020] Using the spin coater (Mikasa, Inc make: 1H-360S), by setting a rotational frequency to 1500rpm, applied to the glass plate in 10 seconds, it was made to dry for 10 minutes at the temperature of 150 degrees C after that, and the light catalytic coating constituent (samples A, B, C, and D) obtained in the aforementioned example and the example of a comparison was used as the test panel (goods). It is ultraviolet-rays quantity of light 1 mW/cm² using these test panels (goods) to a contact angle (inside of Table 1, data for optical irradiation time 0 minute) with water after leaving it in a dark place for 24 hours, and a test panel (goods). The result of having measured the contact angle with water after carrying out the predetermined time exposure of the black light is shown in Table 1. This result showed that the test panel (goods) using the light catalytic coating constituent of this invention was excellent in a contact angle with water being low (it being able to consider as the range which is 0-10 degrees), and the fall of the contact angle under an optical exposure being early, i.e., initial hydrophilization activity, also before an optical exposure.

[0021]

[Table 1]

実験例	試料	光照射時間 (分)					
		0	1 5	3 0	4 5	6 0	7 5
実施例 1	A	2 . 9	0	0	0	0	0
実施例 2	B	4 . 4	0	0	0	0	0
実施例 3	C	3 . 9	0	0	0	0	0
比較例 1	D	1 0 . 4	9 . 6	9 . 5	7 . 2	5 . 5	0

[0022] Next, the result of having held the aforementioned test panel (goods) with which ultraviolet rays were irradiated and the contact angle of water became 0 degree in the dark place is shown in Table 2. This result showed that the test panel (goods) using the light catalytic coating constituent of this invention tends to maintain the condition that a contact angle is low, i.e., excel also in the maintenance nature of hydrophilization activity.

[0023]

[Table 2]

実験例	試料	暗所放置時間 (週)		
		0	2	4
実施例 1	A	0	0	18.9
実施例 2	B	0	0	7.7
実施例 3	C	0	0	18.4
比較例 1	D	0	9.5	26.1

[0024] Next, the dirt component was made to adhere to the aforementioned test panel (goods) with which ultraviolet rays were irradiated and the contact angle of water became 0 degree, and the recoverability of hydrophilization activity was investigated. The spin coater (Mikasa, Inc make: 1H-360S) was used for each test panel (goods) for the xylene solution of 0.005% of linolic acid triglyceride, and it applied in 10 seconds by having set the rotational frequency to 1000rpm, and was made to dry for 10 minutes at the temperature of 100 degrees C after that. These test panels (goods) are used and it is ultraviolet-rays quantity of light 1 mW/cm² to a contact angle with the water before an optical exposure, and a test panel (goods). The result of having measured the contact angle with water after carrying out the predetermined time exposure of the black light is shown in Table 3. This result showed that the test panel (goods) using the light catalytic coating constituent of this invention was excellent in recoverability with the fall of the contact angle under an optical exposure a contact angle with water is low and early, i.e., hydrophilization activity, also before an optical exposure.

[0025]

[Table 3]

実験例	試料	光照射時間 (分)			
		0	15	30	45
実施例 1	A	4.7	0	0	0
比較例 1	D	18.3	7.4	4.3	0

[0026]

[Effect of the Invention] This invention is a light catalytic coating constituent characterized by coming at least to contain a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative, a photocatalyst particle, a binder, and a solvent, can create the photocatalyst film excellent in the photocatalyst function, and can give a photocatalyst function simple on the surface of goods. Especially the light catalytic coating constituent of this invention can form the photocatalyst film excellent in the hydrophilization function (the maintenance nature of initial hydrophilization activity and hydrophilization activity, recoverability of hydrophilization activity), and can obtain goods excellent in antifouling property, fog resistance, etc. Moreover, this invention is goods characterized by coming to form the photocatalyst film on the front face of goods using the aforementioned light catalytic coating constituent, and can be broadly used for industrial use or home use as the goods which have a photocatalyst function, especially goods excellent in the hydrophilization function. Moreover, it is the manufacture approach of the goods which come to form the photocatalyst film which this invention applies the aforementioned light catalytic coating constituent on the surface of goods, or sprays and carries out it, and is subsequently characterized by drying, and a photocatalyst function can be given to the front face of all goods, and the goods which have a photocatalyst function can be manufactured simple.

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TECHNICAL FIELD

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PRIOR ART

[Description of the Prior Art] If the light which has the energy more than the band gap in titanium oxide is irradiated, optical pumping will be carried out and an electron hole and an electron will be generated on a titanium oxide particle front face. Since the electron hole produced especially on the titanium oxide particle front face has very powerful oxidizing power, it can remove deleterious material, such as harmful matter, a malodorous substance, stimulative matter, an environmental pollutant, mold, algae, and bacteria. Thus, if light is irradiated, generally a photocatalyst function, a call, and recent-years research are briskly done in the aforementioned deleterious material removal function which discovers the matter which the electron of a valence band excites by the photocatalyst, the call, and optical pumping. Furthermore, using this photocatalyst function, the front face of goods is made into a hydrophilic property, that it is hard to adhere dirt, it can carry out, or cloudiness can also be prevented, and the application scene of a photocatalyst is spreading.

[0003] Although a photocatalyst is used according to each application in the condition of fine particles, the condition of a Plastic solid, the condition of the sol which distributed the photocatalyst, and the condition of having fixed to the front face of goods, it is used in many cases in the condition of having fixed to the front face of goods from the merit of handling, like scattering and the outflow from the system of reaction being prevented. Furthermore, to use the aforementioned hydrophilization function, it is necessary to form and fix the photocatalyst film in homogeneity on the surface of goods. In order to fix a photocatalyst, since the light catalytic coating constituent which made the binder and the solvent distribute a photocatalyst particle can be applied on the surface of goods or the approach which has sprayed enough and is carried out can form the photocatalyst film in homogeneity, it is a desirable approach.

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EFFECT OF THE INVENTION

[Effect of the Invention] This invention is a light catalytic coating constituent characterized by coming at least to contain a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative, a photocatalyst particle, a binder, and a solvent, can create the photocatalyst film excellent in the photocatalyst function, and can give a photocatalyst function simple on the surface of goods. Especially the light catalytic coating constituent of this invention can form the photocatalyst film excellent in the hydrophilization function (the maintenance nature of initial hydrophilization activity and hydrophilization activity, recoverability of hydrophilization activity), and can obtain goods excellent in antifouling property, fog resistance, etc. Moreover, this invention is goods characterized by coming to form the photocatalyst film on the front face of goods using the aforementioned light catalytic coating constituent, and can be broadly used for industrial use or home use as the goods which have a photocatalyst function, especially goods excellent in the hydrophilization function. Moreover, it is the manufacture approach of the goods which come to form the photocatalyst film which this invention applies the aforementioned light catalytic coating constituent on the surface of goods, or sprays and carries out it, and is subsequently characterized by drying, and a photocatalyst function can be given to the front face of all goods, and the goods which have a photocatalyst function can be manufactured simple.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] If the photocatalyst film is formed using the aforementioned light catalytic coating constituent which comes to contain a photocatalyst particle, a binder, and a solvent, a photocatalyst particle is easy to be covered with a binder, and may be unable to discover an original photocatalyst function easily, and the further improvement is called for.

[Translation done.]

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MEANS

[Means for Solving the Problem] When this invention persons made a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative as a result of examining many things, in order to create the photocatalyst film which can discover the further excellent photocatalyst function, the photocatalyst particle, the binder, and the solvent contain at least and considered as the light catalytic coating constituent, they completed a header and this invention for the desired photocatalyst film being obtained. That is, this invention is to offer the light catalytic coating constituent which forms the photocatalyst film which has the outstanding photocatalyst function. Furthermore, it is in offering the goods which come to form the photocatalyst film using the light catalytic coating constituent, and its manufacture approach.

[0006]

[Embodiment of the Invention] This invention is a light catalytic coating constituent characterized by making it come at least to contain a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative, a photocatalyst particle, a binder, and a solvent. The light catalytic coating constituent of this invention can mix at least a kind of compound and photocatalyst particle which are chosen from the group which consists of dicarboxylic acid and its derivative, a binder, and a solvent with a conventional method, respectively, and can be manufactured.

[0007] A photocatalyst particle is a particle which will discover a photocatalyst function if the light of wavelength with the energy more than the band gap is irradiated, and well-known metallic-compounds semi-conductors, such as titanium oxide, a zinc oxide, tungstic oxide, ferrous oxide, and strontium titanate, can be used combining a single or two sorts or more. It has an especially high photocatalyst function and stable and harmless titanium oxide is chemically desirable. The range of 1-500nm is desirable, and the range which is 1-100nm is more desirable, and since the mean particle diameter of this titanium oxide has the photocatalyst function excellent in the range of 1-10nm, it is [its range which is 1-50nm is still more desirable, and] the most desirable. Furthermore, when at least a kind of metal chosen from the group which consists of V, Fe, Co, nickel, Cu, Zn, Ru, Rh, Pd, Ag, Pt, and Au as the second component on the interior of a photocatalyst particle and/or its front face, and/or metallic compounds are made to contain, since it has a still higher photocatalyst function, it is desirable. As the aforementioned metallic compounds, a metal ion etc. is included in a metaled oxide, a hydroxide, an oxy-hydroxide, a sulfate, a halogenide, a nitrate, and a pan, for example. The content of the second component can be suitably set up with the matter. As a photocatalyst particle which makes an aforementioned metal and/or metallic compounds contain, titanium oxide is desirable. They are about 0.01 - 10 % of the weight, the loadings of a photocatalyst particle have 0.05 - 5 desirable % of the weight in a light catalytic coating constituent, its 0.1 - 5 % of the weight is more desirable to it, and its 0.1 - 1 % of the weight is still more desirable to it. Since it will be hard coming to form the photocatalyst film if [than the above-mentioned range] more [a photocatalyst function will tend to fall if there are few loadings of a photocatalyst particle than the above-mentioned range and], it is not desirable.

[0008] The photocatalyst particle used in this invention is obtained by the well-known approach. As an approach of obtaining titanium oxide, for example, ** sulfuric-acid titanium, sulfuric-acid titanyl. The need is accepted in titanium compounds, such as a titanium chloride and a titanium alkoxide. Under existence of the seed for nucleation The approach and ** need which carry out heating hydrolysis are accepted. Under existence of the seed for nucleation Sulfuric-acid titanium, Alkali is added to titanium compounds, such as sulfuric-acid titanyl, a titanium chloride, and a titanium alkoxide. There is the approach of calcinating or hydrothermal processing the titanium oxide obtained by the approach of the approach of carrying out vapor phase oxidation of the approach and ** titanium chloride to neutralize, the titanium alkoxide, etc., the ** aforementioned **, and ** etc., and since especially the titanium oxide obtained by the approach of the aforementioned ** has the high photocatalyst function, it is desirable. In this invention, it is not asked that the crystal mold is titanium oxide including what is generally called water titanium oxide besides titanium oxide, hydration titanium oxide, metatitanic acid, an alt.titanic acid, hydroxylation titanium, etc. On the interior of a photocatalyst particle, and/or its front face, as the second component, V. In order to make at least a kind of metal chosen from the group which consists of Fe, Co, nickel, Cu, Zn, Ru, Rh, Pd, Ag, Pt, and Au, and/or metallic compounds contain In case a photocatalyst particle is manufactured, this metal and/or these metallic compounds are added. After manufacturing the approach and photocatalyst particle which are made to adsorb, add and this metal and/or these metallic compounds are made to adsorb, it can heat if needed or the approach which has returned enough and is carried out if needed can be used.

[0009] If the thing of the condition of a sol is used, since the smooth photocatalyst film and the photocatalyst film with high transparency will be easy to be obtained, a photocatalyst particle is desirable. For example, in order to obtain a titanium oxide sol, amalgam-decomposition processing of the titanium oxide, such as (1) water titanium oxide, can be carried out with a monobasic acid and its salt, or after adding (2) titanium tetrachlorides in low-temperature water, it can dialyze, or a titanium alkoxide can be added in (3) hydrochloric-acid water solutions, and it can obtain. In the approach of the above (1), water titanium oxide can carry out heating hydrolysis of the titanium compounds, such as water-soluble inorganic titanium compounds, such as for example, sulfuric-acid titanium, sulfuric-acid titanyl, and a titanium tetrachloride, or adds alkali, such as a sodium hydroxide, a potassium hydroxide, and aqueous ammonia, in a titanium compound water solution, neutralizes, and can be obtained. The water titanium oxide obtained by hydrolyzing usually neutralizes this thing with alkali, after it removes solid liquid separation and the sulfuric-acid root which washes, dehydrates and remains inside as much as possible, adds monobasic acids, such as a hydrochloric acid, a nitric acid, an acetic acid, a chloric acid, and the Krol acid, or the salt of those to this dehydrate, and carries out amalgam-decomposition processing. The titanium oxide sol generated by amalgam-decomposition processing contains a monobasic acid or its salt as a distributed stabilizing agent, and usually shows with a pH of three or less acidity. The particle diameter of a titanium oxide particle can be made more detailed by performing heating hydrolysis, lowering neutralization temperature, or making neutralization late.

Thus, if alkali is gradually added to a stable titanium oxide sol by pH of the obtained acid range and pH is raised, a stable titanium oxide sol will be obtained by pH of a neutral region and an alkaline region. An impurity is also removable from the titanium oxide sol of the obtained neutral region and an alkaline region if needed.

[0010] The product obtained as a binder by, for example, hydrolyzing hydrolysis nature silicon compounds, such as alkyl silicate, halogenation silicon, and these partial hydrolysates. Silicon compounds, such as a silica, colloidal silica, water glass, and organopolysiloxane, Phosphate, such as phosphoric acid zinc and aluminium phosphate, heavy phosphate, cement, A kind of binders, such as organic system binders, such as inorganic system binders, such as lime, gypsum, a frit for enamels, glaze for glass lining, and plaster, a fluorine system polymer, and a silicone system polymer, or two sorts or more may be blended. A binder needs to choose the class of binder suitably according to a use scene, and extent and application of a photocatalyst function, in order to deteriorate by the photocatalyst function of a photocatalyst or to decompose. Since the rate of degradation by the photocatalyst function which a photocatalyst particle has, and decomposition is very slow as a binder, the hydrolysis product of hydrolysis nature silicon compounds, such as alkyl silicate, a silicone system polymer, and a fluorine system polymer are desirable. Alkyl silicate is $\text{Si}(\text{OR})_n$ as a general formula. The compound expressed with $(\text{OR})_{2n+2}$ (however, in Si silicon and O show oxygen and R shows an alkyl group.) is said, n is 1-6 and that [R's] whose carbon number is the alkyl group of 1-4 is more desirable at a point with many rates of silicon. They are converted into solid content and are about 10 - 2000 % of the weight to a photocatalyst particle, the loadings of a binder have 25 - 1000 desirable % of the weight, its 25 - 500 % of the weight is more desirable, and its 25 - 250 % of the weight is still more desirable. Since it will become easy for a photocatalyst function to fall if [than the above-mentioned range] more [when there were few loadings of a binder than the above-mentioned range and], it is not desirable.

[0011] As a solvent, an inorganic solvent or organic solvents, and those mixture can be used. As an inorganic solvent, water is desirable. As an organic solvent, alcohols, such as a methanol, ethanol, 2-propanol, and ethylene glycol, and ketones can be used. The thing which comes to contain alcohol from the point of handling nature and coating nature is desirable. The loadings of a solvent can be suitably set up according to workability.

[0012] The light catalytic coating constituent of this invention is made to contain at least a kind of compound chosen from the group which consists of dicarboxylic acid and its derivative. Dicarboxylic acid is an organic compound which has two carboxyl group $\text{COOH}(\text{s})$ in intramolecular, for example, aromatic series dicarboxylic acid, such as aliphatic series partial saturation dicarboxylic acid, such as aliphatic series saturation dicarboxylic acid, such as oxalic acid, a malonic acid, a succinic acid, a glutaric acid, an adipic acid, a pimelic acid, a suberic acid, an azelaic acid, and a sebacic acid, a maleic acid, and a fumaric acid, a phthalic acid, isophthalic acid, and a terephthalic acid, etc. can be used. A dicarboxylic acid derivative is a compound which dicarboxylic acid, such as the esterification object of the aforementioned dicarboxylic acid, a salt of dicarboxylic acid, a dicarboxylic acid anhydride, dicarboxylic acid azide, a dicarboxylic acid amide, and dicarboxylic acid imide, has the change on the structure of an element, and is made into it, for example, dicarboxylic acid methyl, dicarboxylic acid ethyl, dicarboxylic acid propyl, dicarboxylic acid butyl, dicarboxylic acid sodium, dicarboxylic acid ammonium, etc. can be used. Moreover, trade name Rowdy ASORUBU (made in RO - NU PURAN Japan) which blended the goods containing dicarboxylic acid or its derivative, for example, three sorts of dicarboxylic acid ester, may be used. It is about 0.5 - 500 % of the weight to the photocatalyst particle in a light catalytic coating constituent, the content of dicarboxylic acid and its derivative has 5 - 500 desirable % of the weight, its 10 - 500 % of the weight is more desirable, and its 25 - 250 % of the weight is still more desirable. Since the remarkable effectiveness beyond it is hard to accept even if it will be hard to discover the addition effectiveness and will make [more] it than the above-mentioned range, if there are few contents of dicarboxylic acid and its derivative than the above-mentioned range, it is not desirable. In addition, it is guessed that the mechanism of action by containing dicarboxylic acid or its derivative can improve a photocatalyst function, especially a hydrophilization function when it is thought that there is an operation which makes the vapor rate of a solvent slow or promotes the cure rate of a binder as an acid catalyst although it is not yet clear and the photocatalyst film created using the light catalytic coating constituent containing dicarboxylic acid or its derivative becomes porosity. In addition, the light catalytic coating constituent of this invention may be made to contain various additives, such as a dispersant, a surfactant, a curing agent, and a cross linking agent, in addition to at least a kind of compound and photocatalyst particle which are chosen from the group which consists of dicarboxylic acid and its derivative, a binder, and a solvent.

[0013] Next, they are the goods characterized by this invention coming to form the photocatalyst film on the front face of goods using the aforementioned light catalytic coating constituent. As goods, the goods of the metal quality of the materials, such as alloys, such as metals, such as goods of the organic quality of the materials, such as goods of quality of non-equipments, such as ceramics and glass, plastics, rubber, a tree, and paper, and aluminum, and a rope, can be used. It is not restricted to especially the magnitude or the form of goods. The thickness of the photocatalyst film formed on goods can be suitably set up according to an application, for example, can be made into the thickness which is about 0.01-100 micrometers. In order to form the photocatalyst film on goods using the light catalytic coating constituent of this invention It can carry out by applying or spraying a light catalytic coating constituent on goods. Specifically For example, the sinking-in method, a DIP coating method, a spinner coating method, A blade coating method, a roller coating method, a wire bar coating method, It can apply by the usual approaches, such as the reverse-roll-coating method, brush painting, and the sponge applying method, or can spray by the usual approaches, such as a spray coating method. Thus, after applying or spraying, it dries or calcinates and a solvent is removed. As for the temperature of desiccation or baking, it is desirable to carry out at temperature lower than 700 degrees C, and it is more desirable to carry out at the temperature which is room temperature -500 degree C. In this case, since it will become easy for a photocatalyst function to fall if higher than 700 degrees C, it is not desirable. It may decompose or the compound which is chosen from the group which consists of dicarboxylic acid and its derivative in the case of desiccation and baking and which a kind contained at least may evaporate. Furthermore, in order to solidify the used binder if needed, approaches, such as UV irradiation, may be used. In addition, before applying a light catalytic coating constituent to goods or spraying and making it them, by considering organic system binders and the aforementioned inorganic system binders, such as the aforementioned organic system binder, acrylic resin, an epoxy resin, polyester resin, melamine resin, urethane resin, and alkyd resin, as a primer or paint, it may apply to goods beforehand, or you may spray and carry out if needed.

[0014] The goods in which the photocatalyst film of this invention was formed are useful as a photocatalyst. Deleterious material, such as the toxic material which exists in the surroundings of it by making the light of wavelength with the energy more than the band gap of a photocatalyst irradiate, a malodorous substance, the stimulative matter, an environmental pollutant, a bacillus, mold, algae, and bacteria, is removable, and also the front face of goods is made into a hydrophilic property, dirt can be prevented or cloudiness can be prevented. The light containing ultraviolet rays etc. is mentioned as a light to irradiate, for example, light, such as

sunlight, a fluorescent lamp, the black light, a halogen lamp, a xenon flash tube, and a mercury-vapor lamp, can be used. When using titanium oxide as a photocatalyst especially, the light containing a 300-400nm near ultraviolet ray is desirable. An exposure, irradiation time, etc. of light can be suitably set up with the class and amount of the matter to process.

[0015]

[Translation done.]

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EXAMPLE

[Example] Although the example of this invention is shown below, this invention is not limited to these examples.

[0016] Succinic-acid dimethyl and isopropanol were added in the example 1 light catalytic coatings (ST-K03, Ishihara Sangyo [Kaisha, Ltd.] make: what blended the hydrolysis product of a hydrolysis nature silicon compound as a binder, and blended water and alcohol for the sol which contains titanium oxide with a mean particle diameter of 30nm as a photocatalyst as a solvent), and the light catalytic coating constituent (sample A) of this invention was obtained. Titanium oxide concentration is 2 % of the weight, and this sample A is the silicon in a silicon compound SiO₂. The converted amount (solid content) contained succinic-acid dimethyl 245% of the weight to titanium oxide 100% of the weight to titanium oxide.

[0017] In example 2 example 1, except having replaced with succinic-acid dimethyl and having used adipic-acid dimethyl, it processed like the example 1 and the light catalytic coating constituent (sample B) of this invention was obtained. Titanium oxide concentration is 2 % of the weight, and this sample B is the silicon in a silicon compound SiO₂. Adipic-acid dimethyl contained the converted amount (solid content) 245% of the weight to titanium oxide 100% of the weight to titanium oxide.

[0018] In example 3 example 1, except having replaced with succinic-acid dimethyl and having used glutaric-acid dimethyl, it processed like the example 1 and the light catalytic coating constituent (sample C) of this invention was obtained. Titanium oxide concentration is 2 % of the weight, and this sample C is the silicon in a silicon compound SiO₂. The converted amount (solid content) contained glutaric-acid dimethyl 245% of the weight to titanium oxide 100% of the weight to titanium oxide.

[0019] In example of comparison 1 example 1, except not using succinic-acid dimethyl, it processed like the example 1 and the light catalytic coating constituent (sample D) was obtained. Titanium oxide concentration is 2 % of the weight, and this sample D is the silicon in a silicon compound SiO₂. The converted amount (solid content) was contained 100% of the weight to titanium oxide.

[0020] Using the spin coater (Mikasa, Inc make: 1H-360S), by setting a rotational frequency to 1500rpm, applied to the glass plate in 10 seconds, it was made to dry for 10 minutes at the temperature of 150 degrees C after that, and the light catalytic coating constituent (samples A, B, C, and D) obtained in the aforementioned example and the example of a comparison was used as the test panel (goods). It is ultraviolet-rays quantity of light 1 mW/cm² using these test panels (goods) to a contact angle (inside of Table 1, data for optical irradiation time 0 minute) with the water of Ushiro who left it in the dark place for 24 hours, and a test panel (goods). The result of having measured the contact angle with the water of Ushiro who did the predetermined time exposure of the black light is shown in Table 1. This result showed that the test panel (goods) using the light catalytic coating constituent of this invention was excellent in a contact angle with water being low (it being able to consider as the range which is 0-10 degrees), and the fall of the contact angle under an optical exposure being early, i.e., initial hydrophilization activity, also before an optical exposure.

[0021]

[Table 1]

実験例	試料	光照射時間 (分)					
		0	15	30	45	60	75
実施例 1	A	2.9	0	0	0	0	0
実施例 2	B	4.4	0	0	0	0	0
実施例 3	C	3.9	0	0	0	0	0
比較例 1	D	10.4	9.6	9.5	7.2	5.5	0

[0022] Next, the result of having held the aforementioned test panel (goods) with which ultraviolet rays were irradiated and the contact angle of water became 0 degree in the dark place is shown in Table 2. This result showed that the test panel (goods) using the light catalytic coating constituent of this invention tends to maintain the condition that a contact angle is low, i.e., excel also in the maintenance nature of hydrophilization activity.

[0023]

[Table 2]

実験例	試料	暗所放置時間 (週)		
		0	2	4
実施例 1	A	0	0	18.9
実施例 2	B	0	0	7.7
実施例 3	C	0	0	18.4
比較例 1	D	0	9.5	26.1

[0024] Next, the dirt component was made to adhere to the aforementioned test panel (goods) with which ultraviolet rays were irradiated and the contact angle of water became 0 degree, and the recoverability of hydrophilization activity was investigated. The spin coater (Mikasa, Inc make: 1H-360S) was used for each test panel (goods) for the xylene solution of 0.005% of linolic acid triglyceride, and it applied in 10 seconds by having set the rotational frequency to 1000rpm, and was made to dry for 10 minutes at the temperature of 100 degrees C after that. These test panels (goods) are used and it is ultraviolet-rays quantity of light 1 mW/cm² to a contact angle with the water before an optical exposure, and a test panel (goods). The result of having measured the contact angle with the water of Ushiro who did the predetermined time exposure of the black light is shown in Table 3. This result showed that the test panel (goods) using the light catalytic coating constituent of this invention was excellent in recoverability with the fall of the contact angle under an optical exposure a contact angle with water is low and early, i.e., hydrophilization activity, also before an optical exposure.

[0025]

[Table 3]

実験例	試料	光照射時間 (分)			
		0	15	30	45
実施例 1	A	4.7	0	0	0
比較例 1	D	13.3	7.4	4.3	0

[Translation done.]

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(54) 【発明の名称】 光触媒性塗料組成物

(57) 【要約】

【課題】 光触媒粒子、バインダ、溶媒とを含有してなる光触媒性塗料組成物において、優れた光触媒機能を有する光触媒膜を物品の表面に簡便に形成することができる塗料組成物を提供すること。さらに、優れた光触媒機能を有する光触媒膜を形成した物品を提供すること。

【解決手段】 ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物と、光触媒粒子と、バインダと、溶媒とを含有させて、光触媒性塗料組成物とする。さらに、この光触媒性塗料組成物を物品の表面に塗布しあるいは吹き付けし、次いで、乾燥することにより、光触媒膜を形成してなる物品を製造する。

【特許請求の範囲】

【請求項1】ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物と、光触媒粒子と、バインダと、溶媒とを含有してなることを特徴とする光触媒性塗料組成物。

【請求項2】ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物の含有量が光触媒粒子に対して0.5～500重量%であることを特徴とする請求項1に記載の光触媒性塗料組成物。

【請求項3】光触媒粒子の含有量が0.01～10重量%であることを特徴とする請求項1に記載の光触媒性塗料組成物。

【請求項4】光触媒粒子が、1～500nmの範囲の平均粒子径を有する酸化チタンであることを特徴とする請求項1に記載の光触媒性塗料組成物。

【請求項5】バインダが、加水分解性ケイ素化合物の加水分解生成物であることを特徴とする請求項1に記載の光触媒性塗料組成物。

【請求項6】加水分解性ケイ素化合物がSi、O、 OR （但しnは1～6、Rは炭素数が1～4のアルキル基）で表されるアルキルシリケートである20 ことを特徴とする請求項5に記載の光触媒性塗料組成物。

【請求項7】溶媒が、アルコールを含有してなるものであることを特徴とする請求項1に記載の光触媒性塗料組成物。

【請求項8】請求項1に記載の光触媒性塗料組成物を用いて物品の表面上に光触媒膜を形成してなることを特徴とする物品。

【請求項9】請求項1に記載の光触媒性塗料組成物を物品の表面に塗布しあるいは吹き付けし、次いで、乾燥することを特徴とする光触媒膜を形成してなる物品の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、光触媒膜の形成に利用するための光触媒性塗料組成物、光触媒膜を形成した物品およびその製造方法に関する。

【0002】

【従来の技術】酸化チタンにそのバンドギャップ以上のエネルギーを有する光を照射すると、光励起し、酸化チタン粒子表面に正孔と電子が発生する。特に酸化チタン粒子表面に生じた正孔は非常に強力な酸化力を有していることから、有害物質、悪臭物質、刺激性物質、環境汚染物質、黴、藻類、細菌などの有害物を除去できる。このように光を照射すると価電子帯の電子が励起する物質を光触媒と呼び、光励起により発現する前記の有害物除去機能などを一般に光触媒機能と呼び、近年研究が盛んに行われている。さらに、この光触媒機能を利用して、物品の表面を親水性にし、汚れを付着しにくくしたり、50

曇りを防止したりすることもでき、光触媒の適用場面が広がりつつある。

【0003】光触媒は、それぞれの用途に応じて、粉体の状態、成形体の状態、光触媒を分散したゾルの状態、物品の表面に固定した状態で用いられるが、反応系からの飛散や流出を防止できるなどの取扱いのよさから物品の表面に固定した状態で用いられる場合が多い。さらに、前記の親水化機能を利用する場合には、物品の表面に光触媒膜を均一に形成して固定化する必要がある。光触媒を固定化するには、光触媒粒子をバインダ、溶媒に分散させた光触媒性塗料組成物を物品の表面に塗布したり、吹き付けたりする方法が、光触媒膜を均一に形成することができるため好ましい方法である。

【0004】

【発明が解決しようとする課題】光触媒粒子、バインダ、溶媒とを含有してなる前記の光触媒性塗料組成物を用いて光触媒膜を形成すると、光触媒粒子がバインダで覆われやすく、本来の光触媒機能を発現できにくい場合があり、さらなる改善が求められている。

【0005】

【課題を解決するための手段】本発明者らは、より一層優れた光触媒機能を発現できる光触媒膜を作成するために種々検討した結果、ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物と、光触媒粒子と、バインダと、溶媒とを含有させて光触媒性塗料組成物とすると、所望の光触媒膜が得られることを見出し、本発明を完成した。すなわち、本発明は、優れた光触媒機能を有する光触媒膜を形成する光触媒性塗料組成物を提供することにある。さらには、その光触媒性塗料組成物を用いて光触媒膜を形成してなる物品、およびその製造方法を提供することにある。

【0006】

【発明の実施の形態】本発明は、ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物と、光触媒粒子と、バインダと、溶媒とを含有させてなることを特徴とする光触媒性塗料組成物である。本発明の光触媒性塗料組成物は、ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物、光触媒粒子、バインダ、溶媒を常法によりそれぞれ混合して製造することができる。

【0007】光触媒粒子とは、そのバンドギャップ以上のエネルギーを持つ波長の光を照射すると光触媒機能を発現する粒子のことであり、酸化チタン、酸化亜鉛、酸化タングステン、酸化鉄、チタン酸ストロンチウムなどの公知の金属化合物半導体を、単一または二種以上を組み合わせて用いることができる。特に、高い光触媒機能を有し、化学的に安定であり、かつ、無害である酸化チタンが好ましい。この酸化チタンの平均粒子径は、1～500nmの範囲が好ましく、1～100nmの範囲がより好ましく、1～50nmの範囲がさらに好ましく、

1~10nmの範囲が優れた光触媒機能を有するためもっとも好ましい。さらに、光触媒粒子の内部および／またはその表面に、第二成分として、V、Fe、Co、Ni、Cu、Zn、Ru、Rh、Pd、Ag、PtおよびAuからなる群より選ばれる少なくとも一種の金属および／または金属化合物を含有させると、一層高い光触媒機能を有するため好ましい。前記の金属化合物としては、例えば、金属の酸化物、水酸化物、オキシ水酸化物、硫酸塩、ハロゲン化物、硝酸塩、さらには金属イオンなどを含む。第二成分の含有量はその物質により適宜設定できる。前記の金属および／または金属化合物を含有させる光触媒粒子としては、酸化チタンが好ましい。光触媒粒子の配合量は、光触媒性塗料組成物中に0.01~10重量%程度であり、0.05~5重量%が好ましく、0.1~5重量%がより好ましく、0.1~1重量%がさらに好ましい。光触媒粒子の配合量が上記範囲より少ないと、光触媒機能が低下しやすく、また、上記範囲より多いと光触媒膜を形成しにくくなるため好ましくない。

【0008】本発明において用いる光触媒粒子は、公知の方法で得られる。例えば酸化チタンを得る方法としては、①硫酸チタン、硫酸チタニル、塩化チタン、チタンアルコキシドなどのチタン化合物を、必要に応じて核形成用種子の存在下に、加熱加水分解する方法、②必要に応じて核形成用種子の存在下に、硫酸チタン、硫酸チタニル、塩化チタン、チタンアルコキシドなどのチタン化合物にアルカリを添加し、中和する方法、③塩化チタンやチタンアルコキシドなどを気相酸化する方法、④前記①、②の方法で得られた酸化チタンを焼成あるいは水熱処理する方法などがあり、特に、前記①の方法で得られた酸化チタンは、光触媒機能が高いため好ましい。本発明において酸化チタンとは、酸化チタンのほか、含水酸化チタン、水和酸化チタン、メタチタン酸、オルトチタン酸、水酸化チタンなどと一般に呼ばれているものを含み、その結晶型は問わない。光触媒粒子の内部および／またはその表面に、第二成分として、V、Fe、Co、Ni、Cu、Zn、Ru、Rh、Pd、Ag、PtおよびAuからなる群より選ばれる少なくとも一種の金属および／または金属化合物を含有させるには、光触媒粒子を製造する際に該金属および／または該金属化合物を添加し、吸着させる方法、光触媒粒子を製造した後に該金属および／または該金属化合物を添加し、吸着させ、必要に応じて加熱したり、あるいは必要に応じて還元したりする方法を用いることができる。

【0009】光触媒粒子は、ゾルの状態のものを用いると、平滑な光触媒膜や透明性の高い光触媒膜が得られやすいため、好ましい。例えば、酸化チタンゾルを得るには、(1)含水酸化チタンなどの酸化チタンを一塩基酸およびその塩で解膠処理したり、(2)四塩化チタンを低温の水に添加した後透析したり、(3)塩酸水溶液に

チタンアルコキシドを添加したりして得ることができる。上記(1)の方法において、含水酸化チタンは、例えば硫酸チタン、硫酸チタニル、四塩化チタン等の水溶性無機チタン化合物などのチタン化合物を加熱加水分解したり、チタン化合物水溶液に水酸化ナトリウム、水酸化カリウム、アンモニア水などのアルカリを添加し、中和したりして得ることができる。加水分解して得られる含水酸化チタンは、普通このものをアルカリで中和し、固液分離、洗浄、脱水して、内部に残存している硫酸根をできるだけ除去した後この脱水物に塩酸、硝酸、酢酸、塩素酸、クロル酸などの一塩基酸またはその塩を加えて解膠処理する。解膠処理で生成する酸化チタンゾルは、一塩基酸またはその塩を分散安定化剤として含有しており、通常pH3以下の酸性を示す。酸化チタン粒子の粒子径は、加熱加水分解を行ったり、中和温度を下げたり、中和反応を遅くしたりすることによって、より微細なものとすることができる。このようにして得られた酸性域のpHで安定な酸化チタンゾルに、アルカリを徐々に加えpHを上げると、中性域、アルカリ性域のpHで安定な酸化チタンゾルが得られる。得られた中性域、アルカリ性域の酸化チタンゾルから、必要に応じて、不純物を除去することもできる。

【0010】バインダとしては、例えば、アルキルシリケート、ハロゲン化ケイ素およびこれらの部分加水分解物などの加水分解性ケイ素化合物を加水分解して得られた生成物、シリカ、コロイダルシリカ、水ガラス、オルガノポリシロキサンなどのケイ素化合物、リン酸亜鉛、リン酸アルミニウムなどのリン酸塩、重リン酸塩、セメント、石灰、セッコウ、ほうろう用フリット、ガラスライニング用うわぐすり、プラスターなどの無機系バインダ、フッ素系ポリマー、シリコン系ポリマーなどの有機系バインダなどのバインダの一種または二種以上を配合してもよい。バインダは、光触媒の光触媒機能により劣化したり、分解したりするため、使用場面、光触媒機能の程度や用途に応じてバインダの種類を適宜選択する必要がある。バインダとしては、光触媒粒子が持つ光触媒機能による劣化、分解の速度が極めて遅いことから、アルキルシリケートなどの加水分解性ケイ素化合物の加水分解生成物、シリコン系ポリマー、フッ素系ポリマーが好ましい。アルキルシリケートとは、一般式として $Si_nO_{n+1}(OR)_{2n+2}$ (但しSiはケイ素、Oは酸素、Rはアルキル基を示す。)で表される化合物をいい、nが1~6であって、Rは炭素数が1~4のアルキル基であるものがケイ素の割合が多い点でより好ましい。バインダの配合量は、固形分に換算して、光触媒粒子に対して10~2000重量%程度であり、25~1000重量%が好ましく、25~500重量%がより好ましく、25~250重量%がさらに好ましい。バインダの配合量が上記範囲より少ないと光触媒膜としたとき光触媒が脱離しやすく、また、上記範囲より多いと光触

媒機能が低下しやすくなるため好ましくない。

【0011】溶媒としては、無機溶媒または有機溶媒、それらの混合物を用いることができる。無機溶媒としては水が好ましい。有機溶媒としては、メタノール、エタノール、2-プロパノール、エチレングリコール等のアルコール類、ケトン類などを用いることができる。取扱い性、塗工性の点からアルコールを含有してなるものが好ましい。溶媒の配合量は、作業性に応じて適宜設定することができる。

【0012】本発明の光触媒性塗料組成物には、ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物を含有させる。ジカルボン酸とは、分子内にカルボキシル基 COOH を二個持つ有機化合物であり、例えば、シュウ酸、マロン酸、コハク酸、グルタル酸、アジピン酸、ピメリン酸、スベリン酸、アゼライン酸、セバシン酸などの脂肪族飽和ジカルボン酸、マレイン酸、フマル酸などの脂肪族不飽和ジカルボン酸、フタル酸、イソフタル酸、テレフタル酸などの芳香族ジカルボン酸などを用いることができる。ジカルボン酸誘導体とは、前記のジカルボン酸のエステル化物、ジカルボン酸の塩、ジカルボン酸無水物、ジカルボン酸アジド、ジカルボン酸アミド、ジカルボン酸イミドなどのジカルボン酸に小部分の構造上の変化があつてできる化合物のことであり、例えば、ジカルボン酸メチル、ジカルボン酸エチル、ジカルボン酸プロピル、ジカルボン酸ブチル、ジカルボン酸ナトリウム、ジカルボン酸アンモニウムなどを用いることができる。また、ジカルボン酸またはその誘導体を含有した商品、例えば、三種のジカルボン酸エステルを配合した商品名ローディアソルブ（ローヌ・プーラン ジャパン社製）を用いてもよい。ジカルボン酸およびその誘導体の含有量は、光触媒性塗料組成物中の光触媒粒子に対して0.5～500重量%程度であり、5～500重量%が好ましく、10～500重量%がより好ましく、25～250重量%がさらに好ましい。ジカルボン酸およびその誘導体の含有量が上記範囲より少ないと添加効果が発現しにくく、また、上記範囲より多くしてもそれ以上の顕著な効果が認められにくいため好ましくない。なお、ジカルボン酸またはその誘導体を含有することによる作用機構は、未だに明らかになっていないが、溶媒の蒸発速度を遅くしたり、酸触媒としてバインダの硬化速度を促進したりする作用があると考えられ、ジカルボン酸またはその誘導体を含有した光触媒性塗料組成物を用いて作成した光触媒膜が多孔性になることにより、光触媒機能、特に親水化機能が改善できると推察している。なお、本発明の光触媒性塗料組成物には、ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物、光触媒粒子、バインダ、溶媒以外に、分散剤、界面活性剤、硬化剤、架橋剤などの種々の添加剤を含有させてもよい。

【0013】次に、本発明は、前記の光触媒性塗料組成

物を用いて物品の表面上に光触媒膜を形成してなることを特徴とする物品である。物品としては、セラミックス、ガラスなどの無機材質の物品、プラスチック、ゴム、木、紙などの有機材質の物品、アルミニウムなどの金属、鋼などの合金などの金属材質の物品を用いることができる。物品の大きさや形には特に制限されない。物品上に形成される光触媒膜の膜厚は、用途に応じて適宜設定することができ、例えば、0.01～100 μm 程度の膜厚とすることができる。本発明の光触媒性塗料組成物を用いて、物品上に光触媒膜を形成するには、物品に光触媒性塗料組成物を塗布したりあるいは吹き付けたりして行うことができ、具体的には、例えば、含浸法、ディップコーティング法、スピナーコーティング法、ブレードコーティング法、ローラーコーティング法、ワイヤーバーコーティング法、リバースロールコーティング法、刷毛塗り法、スポンジ塗り法などの通常の方法で塗布したり、あるいは、スプレーコーティング法などの通常の方法で吹き付けたりすることができる。このようにして塗布あるいは吹き付けた後、乾燥または焼成して溶媒を除去する。乾燥または焼成の温度は、700℃より低い温度で行うのが好ましく、室温～500℃の温度で行うのがより好ましい。この場合、700℃より高いと光触媒機能が低下しやすくなるため好ましくない。乾燥、焼成の際に、ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の含有した化合物は、分解したり、蒸発したりする場合がある。さらに、必要に応じて、用いたバインダを固化するために、例えば紫外線照射などの方法を用いてもよい。なお、物品に光触媒性塗料組成物を塗布したりあるいは吹き付けたりする前に、必要に応じて、前記の有機系バインダ、アクリル樹脂、エポキシ樹脂、ポリエステル樹脂、メラミン樹脂、ウレタン樹脂、アルキド樹脂などの有機系バインダや前記の無機系バインダをプライマーあるいは塗装として予め物品に塗布したりあるいは吹き付けたりしてもよい。

【0014】本発明の光触媒膜を形成した物品は、光触媒として有用である。光触媒のバンドギャップ以上のエネルギーを持つ波長の光を照射させることにより、その回りに存在する有毒物質、悪臭物質、刺激性物質、環境汚染物質、菌、黴、藻類、細菌などの有害物を除去できるほか、物品の表面を親水性にし、汚れを防止したり、曇りを防止することができる。照射する光としては、紫外線を含有した光などが挙げられ、例えば、太陽光や蛍光灯、ブラックライト、ハロゲンランプ、キセノンフラッシュランプ、水銀灯などの光を用いることができる。特に、光触媒として酸化チタンを用いる場合には、300～400nmの近紫外線を含有した光が好ましい。光の照射量や照射時間などは処理する物質の種類や量によって適宜設定できる。

【0015】

【実施例】以下に本発明の実施例を示すが、本発明はこれらの実施例に限定されるものではない。

【0016】実施例1

光触媒性塗料（ST-K03、石原産業社製：光触媒として平均粒子径30nmの酸化チタンを含有するゾルを、バインダとして加水分解性ケイ素化合物の加水分解生成物を、溶媒として水とアルコールを配合したもの）にコハク酸ジメチル、イソプロパノールを添加して、本発明の光触媒性塗料組成物（試料A）を得た。この試料Aは、酸化チタン濃度が2重量%であり、ケイ素化合物中のケイ素をSiO₂に換算した量（固形分）は酸化チタンに対して100重量%、コハク酸ジメチルは酸化チタンに対して245重量%含有していた。

【0017】実施例2

実施例1において、コハク酸ジメチルに代えてアジピン酸ジメチルを使用したこと以外は実施例1と同様に処理して、本発明の光触媒性塗料組成物（試料B）を得た。この試料Bは、酸化チタン濃度が2重量%であり、ケイ素化合物中のケイ素をSiO₂に換算した量（固形分）は酸化チタンに対して100重量%、アジピン酸ジメチルが酸化チタンに対して245重量%含有していた。

【0018】実施例3

実施例1において、コハク酸ジメチルに代えてグルタル酸ジメチルを使用したこと以外は実施例1と同様に処理して、本発明の光触媒性塗料組成物（試料C）を得た。この試料Cは、酸化チタン濃度が2重量%であり、ケイ素化合物中のケイ素をSiO₂に換算した量（固形分）

は酸化チタンに対して100重量%、グルタル酸ジメチルは酸化チタンに対して245重量%含有していた。

【0019】比較例1

実施例1において、コハク酸ジメチルを用いないこと以外は実施例1と同様に処理して、光触媒性塗料組成物（試料D）を得た。この試料Dは、酸化チタン濃度が2重量%であり、ケイ素化合物中のケイ素をSiO₂に換算した量（固形分）は酸化チタンに対して100重量%含有していた。

【0020】前記の実施例、比較例で得られた光触媒性塗料組成物（試料A、B、C、D）を、スピンコータ（ミカサ社製：1H-360S）を用いて回転数を1500rpmとして10秒でガラス板に塗布し、その後150℃の温度で10分間乾燥させて試験板（物品）とした。これらの試験板（物品）を用いて、暗所で24時間放置した後の水との接触角（表1中、光照射時間0分のデータ）、試験板（物品）に紫外線光量1mW/cm²のブラックライトを所定時間照射した後の水との接触角を測定した結果を表1に示す。この結果から、本発明の光触媒性塗料組成物を用いた試験板（物品）は、光照射前でも水との接触角が低く（0～10°の範囲とすることができ）、光照射下での接触角の低下が早いこと、すなわち、初期親水化活性に優れていることがわかった。

【0021】

【表1】

実験例	試料	光照射時間（分）					
		0	15	30	45	60	75
実施例1	A	2.9	0	0	0	0	0
実施例2	B	4.4	0	0	0	0	0
実施例3	C	3.9	0	0	0	0	0
比較例1	D	10.4	9.6	9.5	7.2	5.5	0

【0022】次に、紫外線を照射して水の接触角が0°になった前記の試験板（物品）を暗所で保持した結果を表2に示す。この結果から、本発明の光触媒性塗料組成物を用いた試験板（物品）は、接触角が低い状態を維持しやすいこと、すなわち、親水化活性の維持性にも優れていることがわかった。

【0023】

【表2】

実験例	試料	暗所放置時間（週）		
		0	2	4
実施例1	A	0	0	18.9
実施例2	B	0	0	7.7
実施例3	C	0	0	18.4
比較例1	D	0	9.5	26.1

【0024】次に、紫外線を照射して水の接触角が0°になった前記の試験板（物品）に、汚れ成分を付着させて、親水化活性の回復性を調べた。それぞれの試験板（物品）に0.005%のリノール酸トリグリセリドのキシレン溶液をスピンコータ（ミカサ社製：1H-360S）を用いて回転数を1000rpmとして10秒で塗布し、その後100℃の温度で10分間乾燥させた。

これらの試験板（物品）を用いて、光照射前の水との接触角、試験板（物品）に紫外線光量 1 mW/cm^2 のブラックライトを所定時間照射した後の水との接触角を測定した結果を表 3 に示す。この結果から、本発明の光触媒性塗料組成物を用いた試験板（物品）は、光照射前で

も水との接触角が低く、光照射下での接触角の低下が早いこと、すなわち、親水化活性の回復性に優れていることがわかった。

【 0 0 2 5 】

【表 3】

実験例	試料	光照射時間（分）			
		0	1 5	3 0	4 5
実施例 1	A	4 . 7	0	0	0
比較例 1	D	1 3 . 3	7 . 4	4 . 3	0

【 0 0 2 6 】

【発明の効果】本発明は、ジカルボン酸およびその誘導体からなる群より選択される少なくとも一種の化合物と、光触媒粒子と、バインダと、溶媒とを含有してなることを特徴とする光触媒性塗料組成物であって、光触媒機能に優れた光触媒膜を作成することができ、光触媒機能を物品の表面に簡便に付与することができる。特に、本発明の光触媒性塗料組成物は、親水化機能（初期親水化活性、親水化活性の維持性、親水化活性の回復性）に優れた光触媒膜を形成することができ、防汚性、防曇性などにも優れた物品を得ることができる。また、本発明

は、前記の光触媒性塗料組成物を用いて物品の表面上に光触媒膜を形成してなることを特徴とする物品であって、光触媒機能を有する物品、特に親水化機能に優れた物品として、工業用、あるいは、家庭用に広範囲に用いることができる。また、本発明は、前記の光触媒性塗料組成物を物品の表面に塗布しあるいは吹き付けし、次いで、乾燥することを特徴とする光触媒膜を形成してなる物品の製造方法であって、あらゆる物品の表面に光触媒機能を付与することができ、光触媒機能を有する物品を簡便に製造することができる。

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